

**Rapid Measurements of Thermodynamic Properties for Alternative Refrigerants
with Vibrating-Tube Densimeter¹**

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ABSTRACT

We have aimed to measure *PVT* properties of alternative refrigerant candidates precisely by means of experimental equipment with a vibrating-tube densimeter. Using this measurement system, we have successfully obtained more than 2,000 *PVT* property data in the liquid-phase, vapor-phase and at saturation boundaries for pure compounds. In addition, more than 1,000 liquid-density data have been obtained for several binary and ternary mixtures. The alternative refrigerants measured in the present study include CF_3OCH_3 (trifluoromethyl methyl ether) and $\text{CF}_3\text{CF}_2\text{OCH}_3$ (pentafluoroethyl methyl ether), which are hydrofluoroethers developed by RITE (the Research Institute of Innovative Technology for the Earth, Japan), and typical hydrocarbons, such as propane, *n*-butane, isobutane and their binary and ternary mixtures. The measurement uncertainties are estimated to be 3 mK for temperature, 0.26 kPa or 0.022 % whichever greater for pressure and 0.07 kg/m^3 or 0.024 % whichever greater for density, respectively. The present measurement system took only a few minutes to get one *PVT* datum, and one or two days to complete the whole measurements at temperatures (240 - 380) K and pressures up to 7 MPa.

Keywords: Isobutane (R-600a); *n*-Butane (R-600); Pentafluoroethyl methyl ether ($\text{CF}_3\text{CF}_2\text{OCH}_3$); Propane (R-290); *PVT* properties; Trifluoromethyl methyl ether (CF_3OCH_3); Vibrating-tube densimeter.

1. INTRODUCTION

In recent years, the refrigeration and air-conditioning field have seen the time of sea change. As is generally known, CFCs (chlorofluorocarbon) and HCFCs (hydrochlorofluorocarbon), which had been used as refrigerant, cleaning, foaming, agents and so on, have been regulated since they have brought about ozone layer depletion. Furthermore, even HFCs (hydrofluorocarbons), which were expected as alternative refrigerants for CFCs and HCFCs because of their zero ozone depletion potential (ODP) and high COP, have been specified as the target for discharge regulation in the COP3 since they have a prominent effect on global warming. Therefore, it is said that development and study of alternative refrigerants that have not only zero ODP but also low global warming potential (GWP) are a pressing need in these days.

In these circumstances, hydrofluoroethers and natural refrigerants are the substances of public attention. Hydrofluoroethers are new refrigerants developed by RITE (the Research Institute of Innovative Technology for the Earth, Japan). They have low GWP and their COP is prospected to be equal to conventional refrigerants, so they are expected to be alternative refrigerants. However, because of very short period to study them, their thermodynamic properties are not well known in the present.

Natural refrigerants, such as HCs (hydrocarbons), ammonia, carbon dioxide and so on, are the most earth-friendly substances since they circulate through a nature in large quantities and their circulation from generation to disappearance is already established. Not to mention that their ODP is zero, their GWP is also vanishingly small. Among some natural refrigerants with such features, HCs such as propane(R-290), *n*-butane(R-600) and isobutane(R-600a) are most expected to be alternative refrigerants. However, they have very few measurement data for thermodynamic properties for long years after 1950's. Hence it is considered that experimental and analytical studies for them must be advanced immediately.

Based on such a situation, the present authors have aimed to measure a set of fundamental thermodynamic properties of alternative refrigerant candidates precisely and rapidly by means of experimental equipment with a vibrating-tube densimeter so as to contribute to development and enhancement of the thermodynamic property database for them. The alternative refrigerants measured in the present study include CF_3OCH_3 (trifluoromethyl methyl ether) and $\text{CF}_3\text{CF}_2\text{OCH}_3$ (pentafluoroethyl methyl ether), which are hydrofluoroethers, and typical hydrocarbons, such as R-290, R-600, R-600a and their binary and ternary mixtures. For these alternative refrigerant candidates, we have successfully obtained more than 2,000 *PVT* property data in the liquid-phase, vapor-phase and at saturation boundaries for pure compounds, and more than 1,000 data in the liquid-phase for several binary and ternary mixtures. These results are introduced in the present paper.

2. A PRINCIPLE OF THE VIBRATING-TUBE DENSIMETER

The principle of a vibrating tube densimeter is in the phenomenon in which the vibration period of the U-shaped tube changes with the densities of the sample fluid enclosed in the tube. Vibrating tube densimeter is the equipment that measures directly the vibration period, τ , of the U-shaped tube completely filled with the sample fluid, and then it relatively computes the densities, ρ , of the sample fluid by applying a principle of a fixed relation between τ and ρ . The outline figure of a vibrating tube densimeter is shown in Fig. 1. When the U-shaped tube completely filled with sample fluid is fixed its ends as shown in Fig. 1 and it is made to vibrate without twists in the direction perpendicular to the page, the sample fluid is restrained by pipe-wall and vibrates as one body, so the influence of viscosity is considered to be sufficiently small because the relative displacement of the U-shaped tube is very small. Therefore, the mode of vibration can be regarded as a normal harmonic motion, and its vibration period, τ , is given by

$$\frac{1}{\tau} = \frac{1}{2\pi} \sqrt{k \left(\frac{1}{m} + \frac{1}{M} \right)} \quad (1)$$

$$m = m_0 + \rho V_0 \quad (2)$$

In Eq. (1), m , M and k represent a corresponding mass of the vibrating tube and a counter weight, and a spring constant of the vibrating tube, respectively. m is equivalent to a sum of the mass of the empty vibrating tube, m_0 , and fluid inside the tube, ρV_0 (ρ : sample density), as shown in Eq. (2). Then Eq. (1) is rewritten to Eq. (3) by introducing a periodical parameter, x , a proportional constant, A , mass ratio, μ , and vibration period under vacuum, τ_0 , as defined in Eqs. (4) through (7).

$$\rho = A \frac{(1 + \mu)x}{1 - \mu x} \quad (3)$$

$$x = (\tau^2 / \tau_0^2) - 1 \quad (4)$$

$$A = m_0 / V_0 \quad (5)$$

$$\mu = m_0 / M \quad (6)$$

$$\tau_0 = 2\pi \sqrt{m_0 / \{k(\mu + 1)\}} \quad (7)$$

It is obvious that the parameter τ_0 defined in Eq. (7) is equivalent to the vibration period when $\rho = 0$, so that τ_0 is simply obtained by measuring the natural frequency of the evacuated tube. As for the parameter A and μ given in Eq. (5) and Eq. (6), they must be determined by measuring some reference fluids whose densities are previously well known from other information source.

3. MEASUREMENT SYSTEM

Figure 2 shows a schematic of the present *PVT* property measurement system. The

measurement equipment is roughly divided into a temperature control-measurement system and a pressure-density measurement system.

The pressure-density measurement unit consists of a vibrating-tube densimeter, a quartz pressure transducer and a variable volume vessel. Pressure and density of the sample are regulated by changing the system inner volume with the variable volume vessel with metallic bellows, and then they are measured with an aid of the densimeter and the pressure gauge. The sample pressure is directly measured by use of a quartz pressure transducer calibrated with a dead-weight piston gauge at different temperatures, so that the data can be recorded automatically and continuously on a computer. The sample density is also logged simultaneously to the computer. Since the vibration period is measured directly by means of the vibrating-tube densimeter hooked to the computer, the operator can immediately confirm the behavior of pressure-density ($P\rho$) locus on the computer screen. The pressure measurement range covers up to 7 MPa and its uncertainty according to the ISO guideline [1] was estimated as,

$$U_P = 0.26 \text{ kPa} + 0.00022P \quad (8)$$

whereas the coverage factor $k = 2$.

For the temperature control-measurement unit, it is considered that silicone oil which was used as a heat-transfer medium in a thermostatic bath and the sample are in a thermal equilibrium state so that the sample temperature can be measured indirectly by controlling the temperature of the silicone oil. The bath temperature is controlled to the target value by means of a PID controller and an associated electronic heater. The temperature is detected by use of a standard platinum resistance thermometer which was calibrated on ITS-90 [2] at the National Metrology Institute of Japan (NMIJ) in 2000 and a thermometer bridge. The present experiments cover (240 - 380) K. Temperature measurement uncertainty was estimated as given in Eq. (9), when the coverage factor, k , is equal to 2.

$$U_T = 3 \text{ mK} \quad (9)$$

4. RESULTS OF CALIBRATION FOR VIBRATING-TUBE DENSIMETER

To calculate density of a sample, three parameters, A , μ and τ_0 , given in Eqs. (5) through (7) are required.

A series of vibration period under vacuum were simply obtained at different temperatures by evacuating the measurement system with a vacuum pump. Taking secular change of the densimeter characteristic and a sample adsorption into consideration, we have used the latest τ_0 data for density calculation.

The mass ratio, μ , given in Eq. (6) can be defined by measuring a couple of density-known fluids with the present measurement system. In this study, water and iso-octane were selected for this purpose and they were measured at 293.15 K and 101.3 kPa by the present measurement system. Then μ was calculated by Eq. (10).

$$\mu = \frac{\rho_{\text{water}} x_{\text{iso-octane}} - \rho_{\text{iso-octane}} x_{\text{water}}}{x_{\text{water}} x_{\text{iso-octane}} (\rho_{\text{water}} - \rho_{\text{iso-octane}})} \quad (10)$$

The density of water, ρ_{water} , was calculated by the IAPWS-95 formulation [3] and that of iso-octane, $\rho_{\text{iso-octane}}$, was reported by Kyoto Electronic Manufacturing, Co. [4], as below.

$$\rho_{\text{water}} = 998.207 \pm 0.001 \text{ kg}\cdot\text{m}^{-3} \quad (11)$$

$$\rho_{\text{iso-octane}} = 691.86 \pm 0.03 \text{ kg}\cdot\text{m}^{-3} \quad (12)$$

From the experimental results, we have determined the mass ratio, μ , as follows.

$$\mu = 0.0030 \pm 0.0005 \quad (13)$$

Then the proportional parameter, A , can be derived from Eq. (3) by measuring density-reference fluid with the present measurement system. In order to obtain A values from Eq. (3), water was selected as the reference fluid as well as the case of μ . Since A is defined as the vibrating-tube mass divided by its inner volume, m_0/V_0 , it decreases under higher pressures or temperatures where the vibrating-tube slightly expands according to the pressure deformation or thermal expansion. To correlate these temperature and pressure dependence of A , a following functional form was employed in the present calibration procedure.

$$A(T, P) = \sum_{i=0}^3 \sum_{j=0}^1 a_{ij} \cdot T^{*i} \cdot P^{*j} \quad (14)$$

$$P^* = (P/\text{kPa})/1000 \quad (15)$$

$$T^* = (T / \text{K})/100 \quad (16)$$

Figure 3 illustrates percent deviation of experimentally obtained values of the proportional parameter, A , derived from the correlation, Eq. (14), on the basis of the present measurements for water. From Fig. 3, it is found that the relative deviation for the parameter A is not greater than $\pm 0.012 \%$ for water except at 320 K which were excluded from the input data to fit the correlation, Eq. (14). Taking density uncertainty of 0.01% for IAPWS-95 formulation [3] at the range of the present interest into account, the reproducibility of Eq. (14) would be considered excellent. In Fig. 3, the percent deviation of A experimentally obtained for methanol were also included. Although there is scatter by about $\pm 0.07 \%$, it is smaller than the claimed uncertainty of the IUPAC thermodynamic table for methanol [5]. Concerning at the lower temperatures even below 273.15 K where the data for water are not available, it

is found that the present correlation has a satisfactory reliability to represent the methanol data with the same performance as that in higher temperature range. Therefore, it can be said that the correlation Eq. (14) possesses a high reproducibility within the present measurement range for temperature, being (240 - 380) K.

By summing up the uncertainties of the parameters, A , μ and τ_0 , we have estimated density-measurement uncertainty of the present study as given in Eq. (17), whereas the coverage factor, k , is equal to 2.

$$U_\rho = 0.07 \text{ kg} \cdot \text{m}^{-3} + 0.00024\rho \quad (17)$$

5. MEASUREMENT RESULTS

We have conducted several serieses of measurement for some pure refrigerants, three hydrocarbons including R-290, R-600 and R-600a, and a couple of hydrofluoroethers, trifluoromethyl methyl ether and pentafluoroethyl methyl ether. Additionally, we have measured liquid-phase PVT_x properties of all the possible binary or ternary combinations of R-290, R-600 and R-600a. In total, flood of data of 2991 points of PVT or PVT_x properties were obtained for above samples. Table I summarizes the present experimental results in detail.

6. DISCUSSION

Due to the page limitation, the present paper will briefly discuss the experimental results for data in liquid phase only. In order to examine an agreement of the present measurements with available thermodynamic property models, relative density deviation was calculated and analyzed in this study.

As for hydrofluoroethers, Fig. 4 shows relative density deviation of the present measurements for pentafluoroethyl methyl ether form the EoS reported by Widiatmo

and Watanabe [6]. The input data for these models are also included in this figure. Note that figure keys show only first author and reported year for simplicity. The present data for pentafluoroethyl methyl ether agree well with those by Ohta et al. [7] and baseline EoS by Widiatmo and Watanabe for temperatures above 260 K. Though the deviation is likely to increase below temperature of 260 K, this would be due to the limited valid range of the EoS.

Concerning trifluoromethyl methyl ether, the comparison introduced similar results. Considering that the present measurements have a similar systematic deviation to earlier measurements used to formulate the EoS by Widiatmo and Watanabe, the present measurements with less uncertainty obtained in wider range than existing data would be valuable contribution to improve the thermodynamic property modeling for these substances.

Concerning pure hydrocarbons, the relative deviation for R-290 from the Helmholtz-type EoS by Miyamoto and Watanabe [10] is shown in Fig. 5. The data of other researchers are also included in the figure and the way of grouping is as well as case for hydrofluoroethers. It is found that the present measurements for R-290 agree with the EoS within ± 0.5 % in relative density except a few points in the vicinity of critical temperature, i.e., 369.811 K [17]. The trend of the deviation for present measurements generally resembles to those by other researchers, but the uncertainties of the present *PVT* data are generally smaller than existing data which were measured many years ago, so that the present measurements may be considered to possess higher reliability than any other data shown in Fig. 5. As for other hydrocarbon compounds such as R-600 and R-600a, we have seen similar results but these are not discussed in the present paper.

Subsequently, similar comparison for the mixtures is discussed. The relative density deviation of present measurements for R-290/600/600a system from the EoS by Miyamoto and Watanabe [18] are shown in Figs. 6 through 9. It is found from these figures that the present measurements for R-290/600/600a system generally agree with

the EoS within ± 0.5 % in density except the data near the theoretical critical points. Concerning hydrocarbon mixture systems of R-290, R-600 and R-600a, the reported thermodynamic property data are limited to a few experimental reports studied in the narrow composition range, so that the present measurements which cover a wide range of composition would be valuable to improve the thermodynamic model for hydrocarbon mixture.

7. CONCLUSIONS

We have successfully achieved rapid and accurate density measurements with vibrating-tube densimeter technique. The required time was reduced to a few minutes for a single *PVT* datum or about two hours for an isothermal measurement series. By using this system, we have measured *PVT* properties for 5 pure substances including trifluoromethyl methyl ether, pentafluoroethyl methyl ether, R-290, R-600 and R-600a, and 12 mixtures for R-290/600/600a system. As a result, about 3,000 points of *PVT* or *PVT_x* data were obtained within a very short period. The present measurements were compared with available thermodynamic models for above listed refrigerants, and we have considered that they would be valuable to improve the thermodynamic model for these important substances used for future thermal-energy conversion systems.

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Table I Particular about the Present Measurement Results

substance	purity mol%	composition mol%	phase	measurement range		No. of data
				T / K	P / MPa	
CF ₃ OCH ₃	99.98	-	liquid	240 - 330	0.5 - 7.0	123
		-	vapor	240 - 330	0.0 - 1.0	70
		-	VLE	240 - 330	0.1 - 1.3	15
CF ₃ CF ₂ OCH ₃	99.99	-	liquid	240 - 380	0.5 - 7.0	202
		-	vapor	290 - 380	0.0 - 1.5	98
		-	VLE	240 - 380	0.0 - 1.7	26
R-290	99.99	-	liquid	240 - 380	0.5 - 7.0	503
		-	vapor	240 - 380	0.0 - 3.4	134
		-	VLE	240 - 380	0.1 - 3.5	41
R-600	99.99	-	liquid	240 - 380	0.5 - 7.0	115
		-	vapor	300 - 380	0.1 - 1.5	27
		-	VLE	240 - 380	0.0 - 1.7	11
R-600a	99.99	-	liquid	240 - 380	0.5 - 7.0	115
		-	vapor	260 - 380	0.0 - 2.1	27
		-	VLE	240 - 380	0.0 - 2.3	11
R-290/600	-	25.0/75.0	liquid	240 - 380	0.5 - 7.0	101
	-	50.0/50.0	liquid	240 - 380	0.5 - 7.0	96
	-	75.0/25.0	liquid	240 - 380	0.5 - 7.0	92
R-290/600a	-	25.0/75.0	liquid	240 - 380	0.5 - 7.0	101
	-	50.0/50.0	liquid	250 - 380	0.5 - 7.0	82
	-	75.0/25.0	liquid	240 - 360	0.5 - 7.0	82
R-600/600a	-	25.0/75.0	liquid	240 - 380	0.5 - 7.0	104
	-	50.0/50.0	liquid	240 - 380	0.5 - 7.0	104
	-	75.0/25.0	liquid	240 - 380	0.5 - 7.0	105
R-290/600/600a	-	34.0/33.0/33.0	liquid	240 - 380	0.5 - 7.0	100
	-	60.0/20.0/20.0	liquid	240 - 380	0.5 - 7.0	93
	-	20.0/60.0/20.0	liquid	240 - 380	0.5 - 7.0	101

VLE = vapor liquid equilibrium

Figure Captions

Fig. 1 The outline figure of a vibrating tube densimeter.

Fig. 2 Schematic diagram of the present experimental apparatus, A, vibrating-tube densimeter; B, variable volume vessel with metallic bellows; C, quartz pressure transducer; D, frequency counter; E, pressure computer; F, computer; G, sample-supplying cylinder; H, pressure regulator; I, nitrogen gas bomb; J, vacuum pump; K, standard platinum resistance thermometer; L, thermometer bridge; M, PID controller; N, thyristor regulator; O, subheater; P, main heater; Q, slide transformer; R, heat exchanger; S, temperature regulator pump; T, cooling bath; U, handy cooler; V1-V7, valves; W, stirrer.

Fig. 3 Reproducibility of the fitted function, Eq. (14), \circ , Water; \times , Methanol.

Fig. 4 Relative density deviation of the present measurements for pentafluoroethyl methyl ether from the EoS by Widiatmo and Watanabe [6], \circ , This work; \triangle , Ohta (2001) [7]; \times , Widiatmo (2001) [8].

Fig. 5 Relative density deviation of the present measurements for R-290 from the EoS by Miyamoto and Watanabe [10], \circ , This work; \square , Dittmar (1962) [11]; \diamond , Ely (1978) [12]; \triangle , Haynes (1983) [13]; \times , Kratzke (1984) [14]; $-$, Reamer (1949) [15]; $+$, Thomas (1982) [16].

Fig. 6 Relative density deviation of the present measurements for the binary system R-290/600 from the EoS by Miyamoto and Watanabe [18], \circ , This work (25/75 mol%); \square , This work (50/50 mol%); \triangle , This work (75/25 mol%); \times , Holcomb (1995) [19].

Fig. 7 Relative density deviation of the present measurements for the binary system R-290/600a from the EoS by Miyamoto and Watanabe [18], ○, This work (25/75 mol%); □, This work (50/50 mol%); △, This work (75/25 mol%); –, Kahre (1973) [20]; ×, Duarte-Garza (1999) [21]; +, Thompson (1980) [22].

Fig. 8 Relative density deviation of the present measurements for the binary system R-600/600a from the EoS by Miyamoto and Watanabe [18], ○, This work (25/75 mol%); □, This work (50/50 mol%); △, This work (75/25 mol%); ×, Kahre (1973) [20].

Fig. 9 Relative density deviation of the present measurements for the ternary system R-290/600/600a from the EoS by Miyamoto and Watanabe [18], ○, This work (60/20/20 mol%); □, This work (20/60/20 mol%); △, This work (34/33/33 mol%).

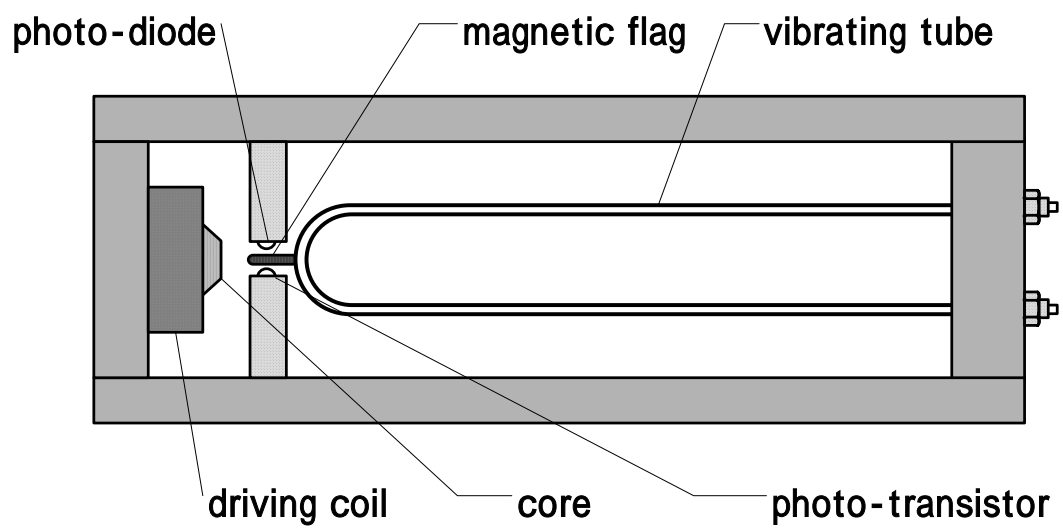


Fig. 1

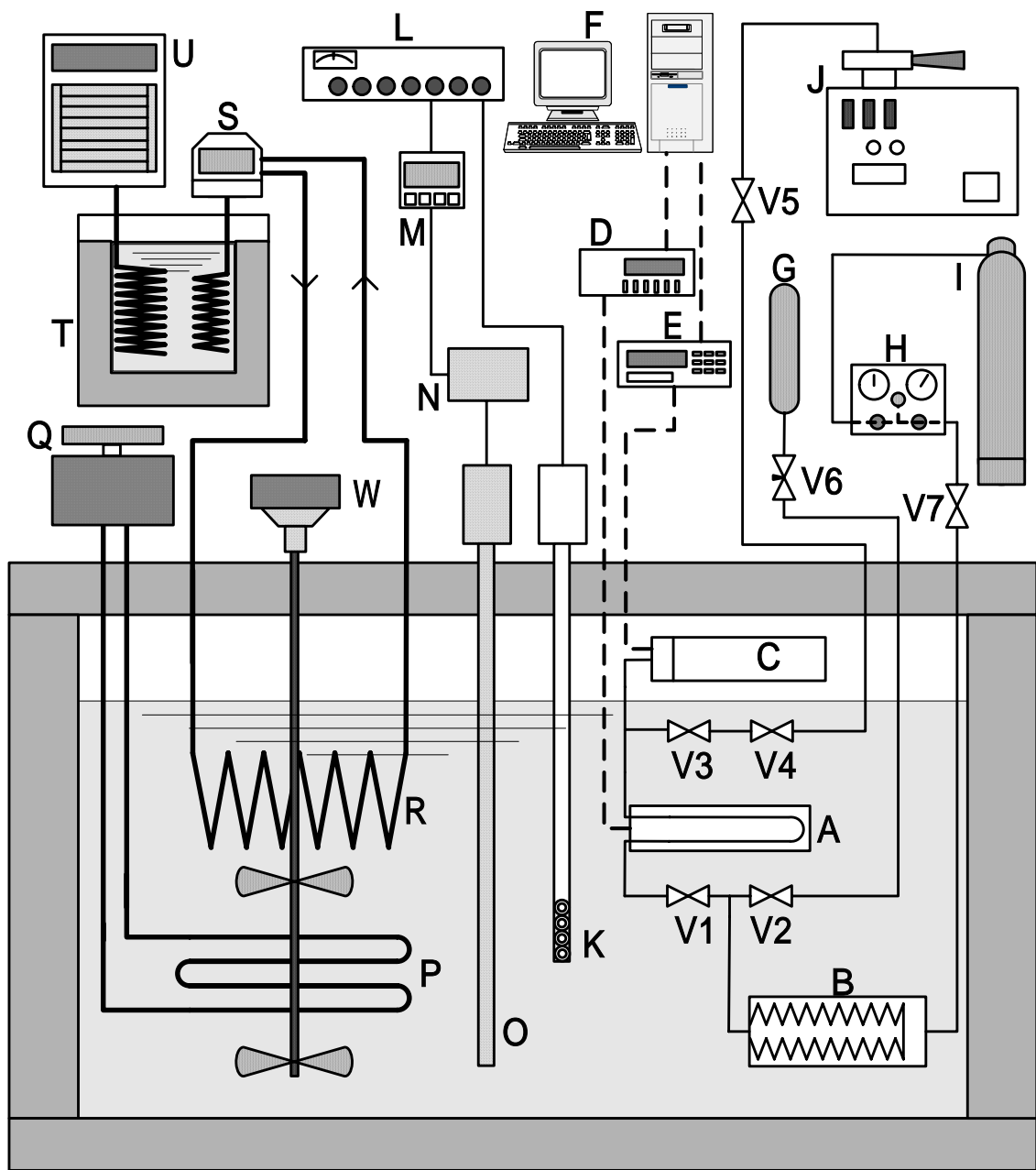
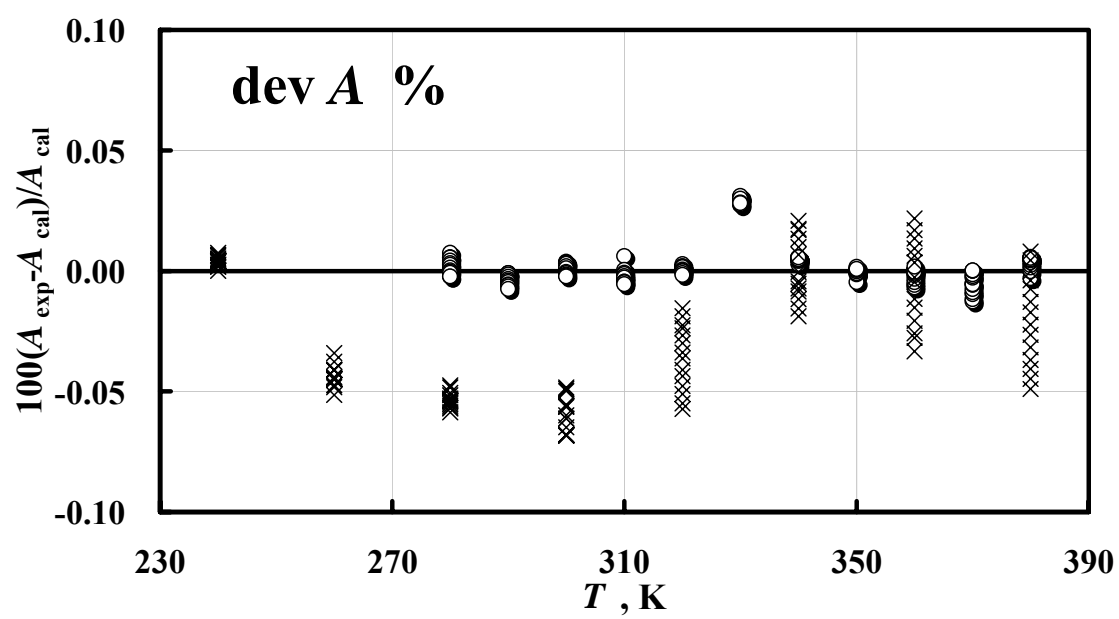


Fig. 2



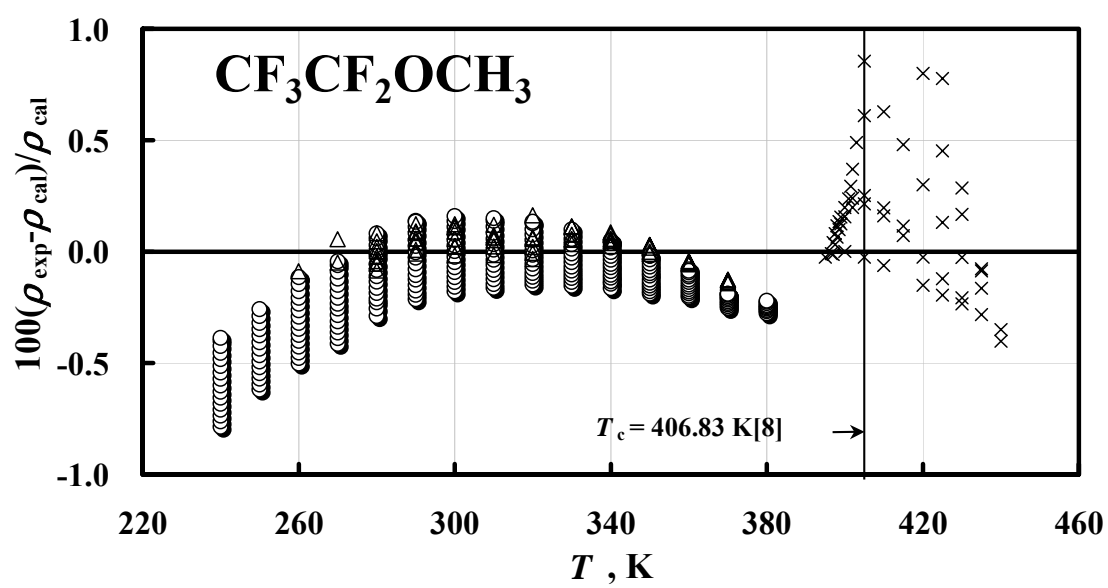


Fig. 4

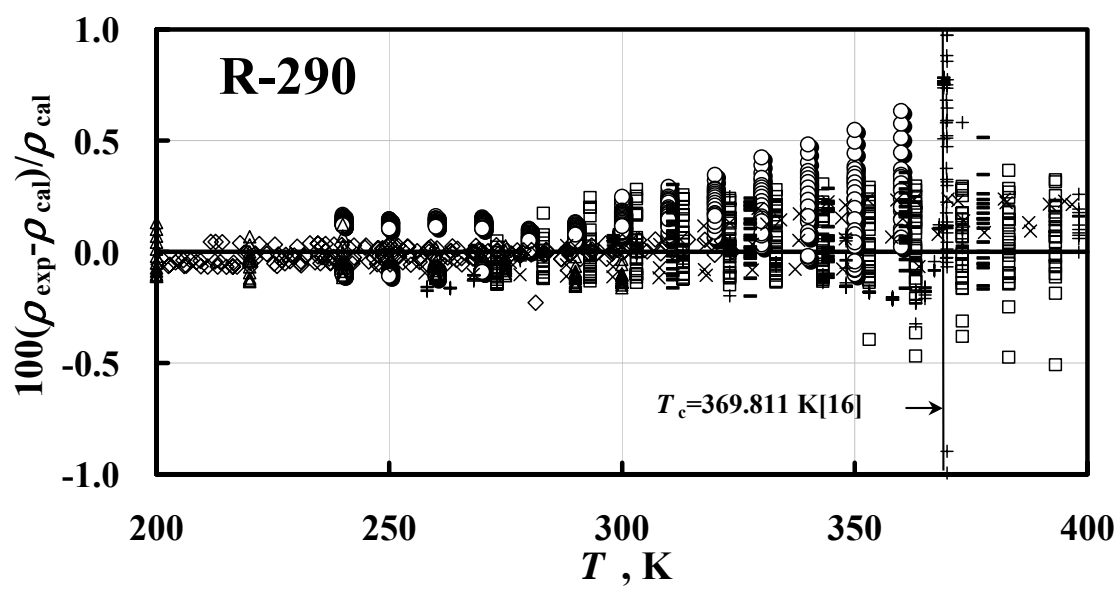


Fig. 5

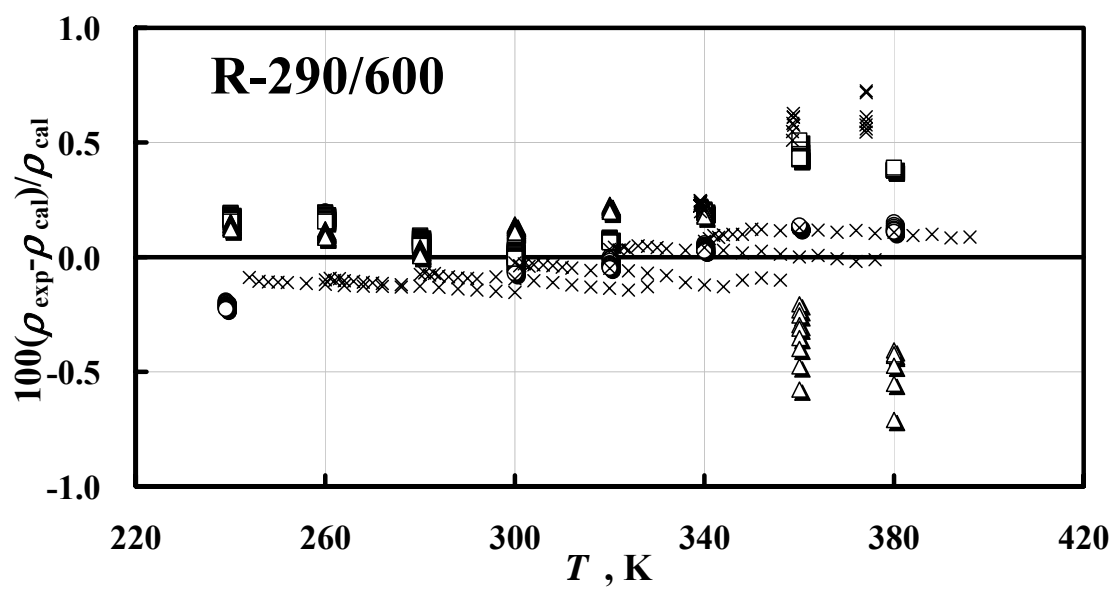


Fig. 6

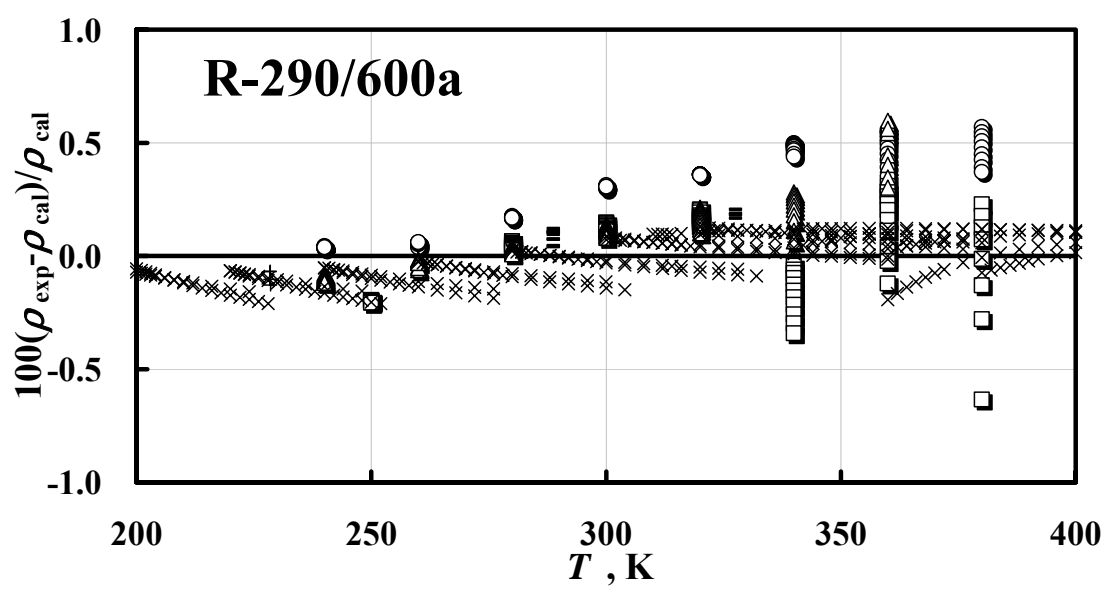


Fig. 7

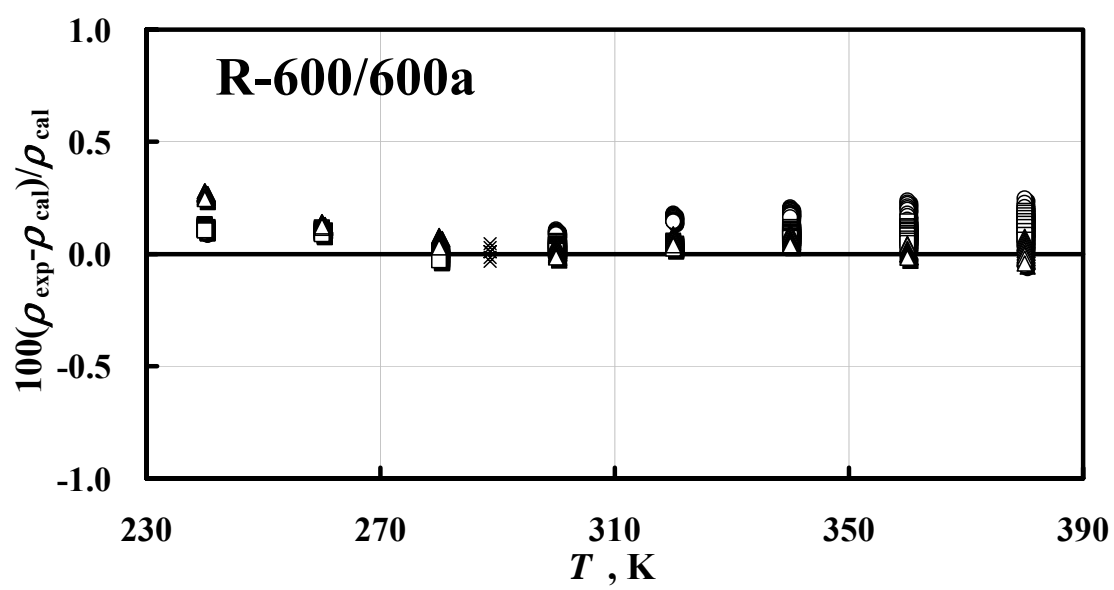


Fig. 8

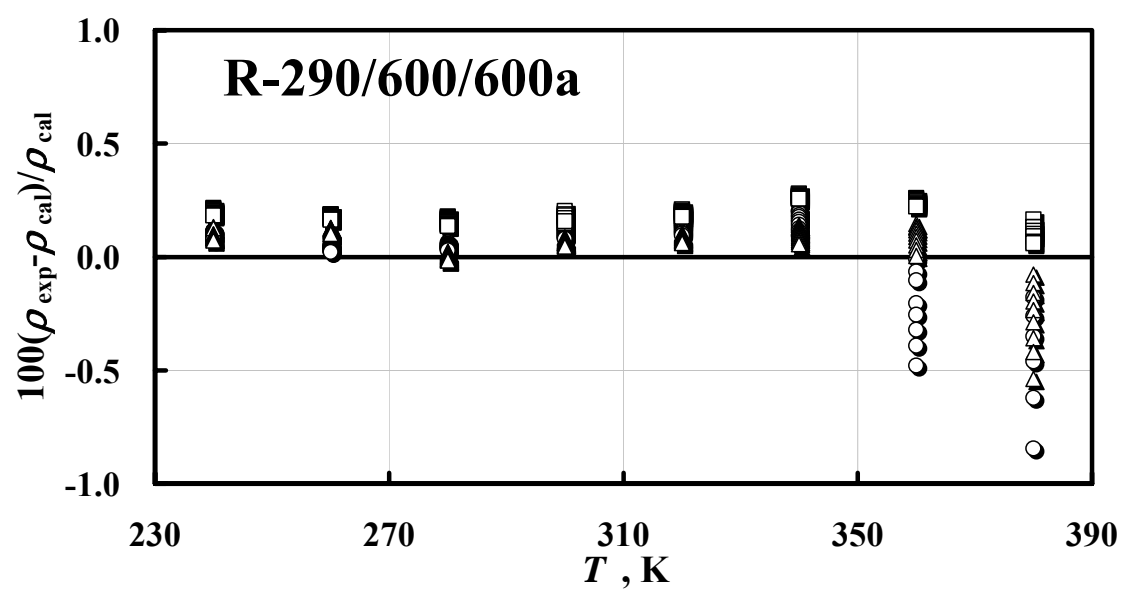


Fig. 9